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Anharmonic model of instability evolution near the bcc→hcp phase transition in Zr

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A local minimum is observed on the full-potential linear-muffin-tin-orbital curve of total energy versus the amplitude of atomic displacements corresponding to transverse $[1\bar{1}0]$ vibrations at the N point of the Brillouin zone in Zr. The temperature dependence of the inelastic one-phonon neutron-scattering spectra is calculated within the framework of a modified pseudoharmonic approximation. The appearance of the spectrum fine structure with decreasing temperature is associated with the intermediate phase phonon whose frequency is close to that of the a phonon of hcp Zr. [S0163-1829(98)06405-4]

In a microscopic description of martensitic phase transitions from first principles, the model based on the study of the peculiarities of the lattice dynamics has been intensively used in the last ten years.[1] The current status of the band theory and the development of consistent *ab initio* methods for calculating the electronic structure of crystals open the way for theoretical investigation of the lattice dynamics.[2] The simplest way of calculating the selected vibrational modes is the ''frozen-phonon'' technique[3] where the effective phonon potential is defined in terms of the difference in total energy between the perfect and distorted lattices for various magnitudes of the atomic displacement amplitude. Knowing this potential, one finds the frequency of the phonon having a wave vector commensurate with the reciprocal-lattice vector.

The first-order bcc→hcp transition in Zr at $T=1136$ K is martensitic. Previously, this transition was suggested to occur through atomic displacements corresponding to the transverse N phonon of bcc symmetry with a wave vector $\mathbf{q}=(2\pi/a)(\frac{1}{2},\frac{1}{2},0)$ (see, e.g., Ref. 4). The calculation of the N-phonon frequency within the harmonic approximation yielded an imaginary frequency, which indicates that this phase is unstable for Zr at low temperatures[5]. Allowance for the anharmonicity effects makes it possible to stabilize the bcc structure at high temperatures.[6] In our opinion, however, the conventional approaches are not suitable for describing the dynamics of strongly anharmonic modes. The goal of our work is to calculate the effective potential for the N phonon by the full-potential linear-muffin-tin-orbital (FP-LMTO) method and then to allow for the anharmonicity effects in the framework of the modified self-consistent phonon approximation.[7]

The total energy for three observed phases of Zr was calculated from first principles[8] by the FP-LMTO method[9] with the use of the generalized gradient approximation[10] for the exchange-correlation energy. For all crystal structures of Zr, the MT sphere radii were chosen to be equal and corresponding to one of the two types of ω phase atoms at the site (0,0,0): $r_{\mathrm{MT}}=2.747$ a.u. The magnitudes of nonoverlapping MT radii should be such as to enable atomic displacements in the cell. Upon calculation of the equilibrium lattice constant $a_{\mathrm{eq}}=6.7724$ a.u. of bcc Zr, we can construct for it a four-atom supercell. The vibrational mode corresponding to the N phonon can be defined through a distorted cell with four displaced atoms. The displacements correspond to transverse vibrations in a plane perpendicular to the z axis. The original cubic symmetry of the bcc lattice is reduced to D_{2h}^{17} with eight group operations,[11] and the real-space unit cell is doubled. Integration over the irreducible part of the Brillouin zone (BZ) is performed using 512 **k** points. The maximum values of the angular momentum l in the expansion of basis functions in spherical harmonics inside the MT spheres, in the re-expansion of MT orbitals outside the MT spheres, as well as in the crystalline potential and charge-density expansions are equal to 2, 4, and 8, respectively. Good convergence is ensured by a double set of basis orbitals with fixed and properly spaced κ's (κ^2 is the mean kinetic energy of an electron in the interstitial region).

The effective potential $U(x)$ which represents the difference in total energy between the perfect and distorted supercell of bcc Zr as a function of the amplitude of reduced atomic displacements $x=u/a$ corresponding to transverse vibrations $[1\bar{1}0]$ at the N point of the BZ is shown in Fig. 1. The calculated curve is similar to that obtained in Ref. 6. The maximum of $U(x)$ at $x=0$ results in the following relation for the frequency: $\omega^2 \sim [\partial^2 U(x)/\partial x^2]_{x=0} < 0$, which implies the instability of the bcc phase at low temperatures. In what follows we use the bcc-hcp phase-transition model from Ref. 4 to interpret the results obtained. According to this model, the atomic displacements along the $[1\bar{1}0]$ direction reduce the space symmetry from O_h^9 to D_{2h}^{17}. For the atomic displacement amplitude $x=\sqrt{2}/12$, the problem symmetry turns out to be D_{6h}^4 (see Ref. 4), with further distortion leading to the formation of the hcp phase whose z axis is directed along $[110]_{\mathrm{bcc}}$. In this case the interplanar spacings remain actually unchanged and the A point in the hcp BZ corresponds to the N point in the bcc BZ. Within the framework of such a model, it is reasonable to associate the minima on the $U(x)$ curve with the intermediate D_{6h}^4 structure of lower energy. It should be mentioned that the minima of the calculated potential do not quantitatively agree with the reduced atomic displacement $x=\sqrt{2}/12$ corresponding to the D_{6h}^4 structure. This is due to the fact that the first-principles calculation of $U(x)$ at $T=0$ was performed for the theoretical equilibrium lattice constant which is less than the experimental one, and

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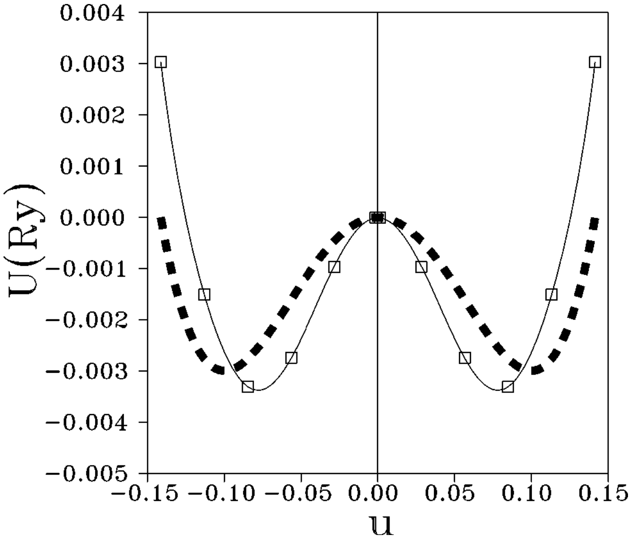

FIG. 1. Lattice potential versus the atomic displacement amplitude $u_{\mathbf{q}}$ (in units of the lattice constant) for transverse vibrations of the normal N mode. Open squares correspond to the calculated values, and the solid line shows the polynomial approximation. Dashed line corresponds to $U(x)$ from Ref. 6.

the entropy contribution was not taken into account. Hence, we cannot expect the phonon frequency to agree quantitatively with the experimental data. (Note that the calculation was conducted with a value of the lattice constant less than the real one, so we should expect overestimating the phonon frequencies).

The main experimental tool for investigating the phonon frequencies is the slow neutron scattering on lattice vibrations. The position and width of the peak of the differential section of one-phonon inelastic coherent neutron scattering determine the phonon frequency and lifetime. The intensity of the spectral line is proportional to the imaginary part of the one-phonon Green function — the spectral density $g_q(\omega,T)$:[12]

$$I_q(\omega,T)\sim g_q(\omega,T)=\frac{1}{\pi}\frac{\Gamma(\omega_q,T)}{[\omega-\tilde{\omega}_q(T)]^2+\Gamma^2(\omega_q,T)}. \quad (1)$$

Here $\tilde{\omega}_q(T)$ is the renormalized phonon frequency; $\Gamma(\omega_q,T)$ is the phonon attenuation due to various scattering processes. We concentrate on the anharmonicity effects which seem to govern the phase transitions that can be described within the soft-mode model. As a rule, when describing the effect of anharmonicity on the position and shape of the phonon spectrum line, one restricts oneself to taking into account the third- and fourth-order anharmonic terms of perturbation theory.[12] For strongly anharmonic systems being unstable in the harmonic approximation, this approach is hardly valid.

In this work we use a modified pseudoharmonic approximation developed in Ref. 7 for anharmonic quasilocal modes associated with the low-frequency vibrations of the defect. Such an approach is also suitable for the delocalized phonon modes, since it implies that the dynamics of a phonon mode weakly interacting with a thermostat can be described by the Langevin equation which in this case involves the phonon-mode amplitude rather than the defect coordinate. Recently, the possibility of such a description of the inelastic neutron-scattering spectra temperature dependence has been discussed in Ref. 13, where the Langevin and the corresponding Fokker-Planck equations have been solved numerically. The numerical solution of stochastic differential equations is rather complicated and requires great computational efforts for any new form of the potential.[14] That is why it seems reasonable to use approximate techniques, like the modified pseudoharmonic approximation[7] allowing for fluctuations of the mean energy of a vibrational mode interacting with a thermostat.

In Ref. 7, a new variable E denoting the energy averaged over the characteristic period of the oscillations in an anharmonic potential is introduced. This is a random variable with the equilibrium distribution function:

$$\rho(E)=\exp(-E/T)/T \quad (2)$$

and the mean value $\langle E\rangle=T$. The characteristic time of variation of E is $\tau_E\sim 1/\Gamma \gg 1/\omega_q$, i.e., the variable is slow as compared to the oscillation period. Therefore the hierarchy of times is realized here, which allows us to define the correlator $\langle u^2\rangle$ and to use the pseudoharmonic approximation for each E.[15,7] The partial density $g_q(\omega)$ can now be found by averaging expression (1) with distribution function $\rho(E)$.

The result obtained in this approach for a symmetric two-well potential described by a fourth-degree polynomial can be resumed as follows:[7] at all temperatures, there exists a probability of basic (localized near the potential minima) vibrations with frequencies ω_b close to the principal frequency ω_0 $[\omega_0^2=(1/a^2)\partial^2U(x)/\partial x^2|_{x=x_{\mathrm{min}}}]$, and excited (overbarrier) vibrations with $\omega_e\simeq\omega_0/2$. With increasing temperature the portion of basic vibrations diminishes $c_b=1-\exp(-E_c/T)$ (E_c is the energy of the ‘‘local transition’’[15]), and the share of the excited ones increases $c_e=1-c_b$. New harmonics therewith arise, which leads to a shift of the peaks (the basic vibration peak shifts towards the low-frequency range, and the excited peak—towards the high-frequency one) and to their anharmonic broadening. The above results are in good agreement with some other investigations,[13,17] which allows this approximation to be used in describing the dynamics of an anharmonic mode with arbitrary potential and oscillator attenuation.

To calculate $\omega(e)$ we approximate the computed values of $U(x)$ by the polynomials of different degrees— 4,6,8,10. At the temperatures discussed the results do not depend qualitatively on the polynomial degree, below we show only the results obtained for the eighth-degree polynomial which describes quite well the behavior of $U(x)$ for all considered values of x. This potential is characterized by a barrier height $e_b=3.45$ mRy, a ‘‘local transition’’ energy $e_c\simeq 0.7E_b$ and a principal frequency $\nu_0=\omega_0/2\pi=3.51$ THz. We assume that the principal frequency corresponds to that of the intermediate phase phonon and is close to the frequency of the hcp A phonon. The minimum frequency of the excited vibrations, approaching that of the high-temperature bcc phase N phonon, is about half as large as ν_0. The ratio between the frequencies of bcc N and hcp A phonons for Zr agrees with the observed one, although their absolute magnitudes exceed the experimental values by a factor of 1.5–2 (Refs. 16,17).

In spectrum calculations, it is necessary to specify the phonon nucleator attenuation at any energy E. We confine ourselves to the processes of soft-phonon scattering by electrons and phonons. The nucleator attenuation is assumed to depend only on $\langle E\rangle = T$, the mean value of the variable E:

$$\Gamma(\omega_q,E)=\Gamma(\omega_q,T)=\Gamma_e(\omega_q,T)+\Gamma_p(\omega_q,T). \quad (3)$$

At high temperatures, the attenuation due to electron-phonon interaction, Γ_e, is frequency and temperature independent, and the attenuation caused by phonon-phonon interaction is proportional in this limit to the temperature:[18] $\Gamma_{p,i}=\Gamma_{0,i}T/E_b$. Here the subscript $i=b,e$ determining the type of vibrations allows us to take account of the difference in attenuation between the basic b and excited e vibrations. Since the intermediate phase is of nonequilibrium character, it is reasonable to suppose that the phonon-phonon interaction in this phase is stronger than in the high-temperature equilibrium bcc phase, i.e., the attenuation of basic vibrations is larger than that of the excited ones. Figure 2 displays the calculated functions $g_q(\omega)$ for $\Gamma_{p,b}=2\Gamma_{p,e}\simeq 0.046\omega_0$ at different temperatures. The low-temperature curve (1) exhibits the fine structure of the spectrum consisting of a high-frequency basic peak and a low-frequency excited one. The stronger attenuation of the basic vibrations at high temperatures results in smearing of the high-frequency peak, the spectrum fine structure is no longer revealed, and curve 2 qualitatively corresponds to the experimental one.[16]

Within the framework of the modified pseudoharmonic approximation the spectrum density of the phonon line is represented by two peaks corresponding to basic (localized near the minima) and excited (overbarrier) vibrations. At high temperatures (in the range of the existence of bcc Zr), the portion of strongly attenuated basic vibrations is small, and the one-phonon inelastic neutron-scattering spectrum constitutes a broad peak which is mainly due to the excited vibrations. In our opinion, the N-phonon frequency in the high-temperature bcc phase is determined by the position of this peak. In the model considered, the evolution of instability in the bcc phase is connected with the increase of the share of high-frequency basic vibrations corresponding to the intermediate D_{6h}^4 phase. We believe the frequency of these vibrations to be close to that of the hcp A phonon. The suggested model of the instability evolution for the martensitic transformation substantially differs from that proposed in Ref. 13 whose authors associate the high-frequency basic vibrations with the N phonon of the high-temperature bcc phase, interpreting the formation of the fine structure of inelastic neutron-scattering spectra with increasing temperature as a manifestation of the ''nonphonon'' behavior of the system. The inelastic neutron-scattering experiments carried out in a wide temperature range of the bcc Zr existence would confirm the validity of our model.

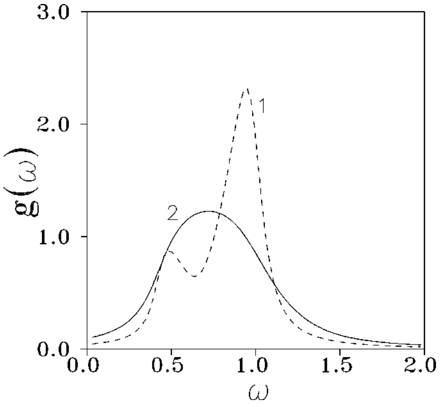

FIG. 2. Spectrum density of the transverse N phonon at two temperatures: $T=0.5E_b$ (1); $T=2.5E_b$ (2). The frequency is expressed in terms of the principal frequency ω_0.

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